Indian J. Phys. 64B (1), 42-49 (1990)

Statistical mechanical studies of polystyrene latex dispersions in water and in very dilute NaCl solution

R V Gopala Rao and Debasis Debnath
Physical Chemistry Section, Jadavpur University, Calcutta-700 032, India

Received 11 May 1989, accepted 4 August 1989

Abstract: Using square-well potential and Verwey-Overbeek (VO) potential function as the basic description, the liquid state properties of polystyrene latex in water and in dilute NaCl solutions are derived respectively. The structure factors of these latex particles predicted by this two model are compared with results obtained from small angle neutron scattering experiments. Fourier inversion of structure factors have been performed to obtain the radial distribution function (RDF) and from these, RDF's co-ordination numbers of the latex particles have been computed. The surface potential ψ_s of the latex in salt solution has been determined from the amplitude (A) of the VO potential. The results are in good agreement, suggests that the structure of such high polymer latex systems can be satisfactorily represented by model potentials.

Keywords: Latex molecule, structure factor, interaction potential, radial distribution function, surface potential.

PACS Nos: 61.20 GY, 61.25 Hq.

1. Introduction

In recent years, extensive studies have been carried out on various synthetic and high polymeric compounds such as polyacrylates (Ise *et al* 1980), polystyrene latex (Cebula *et al* 1983), PMMA latex (Nieuwenhuis *et al* 1979) by small angle X-ray scattering, small angle neutron scattering and light scattering techniques. Therefore, it is important to see how the well known liquid state statistical mechanical equations predict the various properties of these high molecular weight systems. In this communication, perturbation theory has been applied to obtain the structural properties of monodisperse polystyrene latex in-water solution (Cebula *et al* 1983). In absence of salt solution, the interaction potential for polystyrene latex particles is modelled as a repulsive hard sphere to which an attractive square-well potential is added (Jansen *et al* 1986, Rouw and Kruif 1988, Reddy and Murthy 1982) and this model has been applied successfully to generate the structure factor for the present system. In salt solution, the repulsive Verwey-Overbeek (VO) potential (Verwey and Overbeek 1948, Klein and Hess 1983,

Megen and Snook 1983, Snook and Megen 1984) has been used to explain the structure of polystyrene latex as a function of ionic composition of the suspended medium. Here the repulsions at larger separation is due to overlap of electrical double layers and the results are qualitatively consistent with VO theory. Since polystyrene is a molecule with side benzene rings, it is highly asymmetric and hence polar in character. So the surface potential and basic surface charge density of the latex molecule can be obtained from the amplitude (A) of the VO potential.

2. Evaluation of structure factor of polystyrene latex in water and in dilute NaCl solution

As pointed out earlier, here we use the square-well potential function to evaluate the structure factor of polystyrene latex in water solution. The structure factor $S(k)$ is related to the total correlation in the momentum space as

$$S(k)=1+\rho\tilde{h}(k) \tag{1}$$

and

$$\tilde{h}(k)=\frac{\tilde{C}(k)}{1-\rho\tilde{C}(k)} \tag{2}$$

Here $\tilde{h}(k)$ is Fourier Transform of $h(r)$, the total correlation function and $\tilde{C}(k)$ is that of $C(r)$ the direct correlation function (DCF). The details of $S(k)$ with a square well potential function has been described extensively elsewhere (Rao and Murthy 1974, Rao and Sen 1976) and will not be repeated here.

In presence of dilute NaCl solution, the interaction behaviour of latex particles is tested by calculating the structure factor $S(k)$ with the Verwey-Overbeek two particle potential (VO) and can be written as

$$V(r)=\infty \quad r\leqslant\sigma \tag{3}$$

$$=A\frac{e^{-\chi r}}{r} \quad r>\sigma \tag{4}$$

In the hard core region we use the Wertheim-Thiele hard sphere (Wertheim 1963, Thiele 1963) solution and outside the core the above VO potential function as given in eq. (4). Here

$$A=\epsilon_0\epsilon_r\sigma^2\psi_\delta^2 e^{\chi\sigma} \tag{5}$$

where ϵ_0 is the permittivity of free space and ϵ_r is the relative permittivity of the medium. ψ_δ is the surface potential, χ is the Debye-Hückel screening parameter which is given by

$$\chi^2=\frac{2e^2NC_i10^3}{\epsilon_0\epsilon_r k_BT} \tag{6}$$

Here e is the fundamental electronic charge, N is the Avogadro's number, C_t is the concentration of the electrolyte in mol. dm^{-3} and rest of the symbols have their usual connotation. Thus, we obtain

$$\tilde{C}_T(k) = \tilde{C}_{hs}(k) + \tilde{C}_y(k) \tag{7}$$

where $\tilde{C}_y(k)$ is the Fourier Transform of the VO potential outside the core under the MSA assumption. The total correlation function $\tilde{C}_T(k)$, so obtained is given by

$$\begin{aligned}\rho\tilde{C}_T(k) = & \left\{-\frac{24\eta(1+2\eta)^2}{(1-\eta)^4}\right\} \times \left\{\frac{\sin k\sigma - k\sigma\cos k\sigma}{(k\sigma)^3}\right\} + \left\{\frac{144\,\eta^2(1+\eta/2)^2}{(1-\eta)^4}\right\} \\ & \times \{(-k^2\sigma^2\cos k\sigma + 2\,k\sigma\sin k\sigma + 2\cos k\sigma - 2)/(k\sigma)^4\} \\ & + \left\{-\frac{12\,\eta^2(1+2\,\eta)^2}{(1-\eta)^4}\right\} \times \{(-k^4\sigma^4\cos k\sigma + 4k^3\sigma^3\sin k\sigma \\ & + 12\,k^2\sigma^2\cos k\sigma - 24\,k\sigma\sin k\sigma - 24\cos k\sigma + 24)/(k\sigma)^6\} \\ & - \frac{24\,\eta A}{k_B T k\sigma^3} \times \frac{1}{(\chi^2+k^2)} \times e^{-\chi\sigma}(\chi\sin k\sigma + k\cos k\sigma)\end{aligned} \tag{8}$$

Hence, $S(k)$ is obtained from the following equation

$$S(k) = [1 - \rho\tilde{C}_T(k)]^{-1} \tag{9}$$

where, ρ is number density of the solution. The potential parameters have been obtained from the experimental peak position of $S(k)$ and are given in Table 1.

Table 1 : Potential parameters used for polystyrene latex in water and in 10^{-4} mol dm^{-3} NaCl solution.

Volume fraction (η)	σ (Å)	ϵ/k_B (°K)	λ	A (erg Å)	χ (Å^{-1})
In water					
0.04	626.0	1605.0	1.56	—	—
0.08	518.0	965.0	1.56	—	—
0.13	406.0	595.0	1.56	—	—
In NaCl					
0.01	820.0	—	—	0.52×10^{20}	0.104
0.04	624.0	—	—	0.40×10^{20}	0.104
0.13	400.0	—	—	0.65×10^{9}	0.104

χ has been calculated from eq (6), $T = 298$ °K

Similar approach was followed by other workers (Ascroft and Leckner 1966, Rao and Murthy 1975, Klein and Hess 1983, Cebula *et al* 1983). The structure factor of polystyrene latex, along with the experimental results (Cebula *et al* 1983) in water and 10^{-4} mol dm^{-3} NaCl solutions are shown in Figure 1. Structural

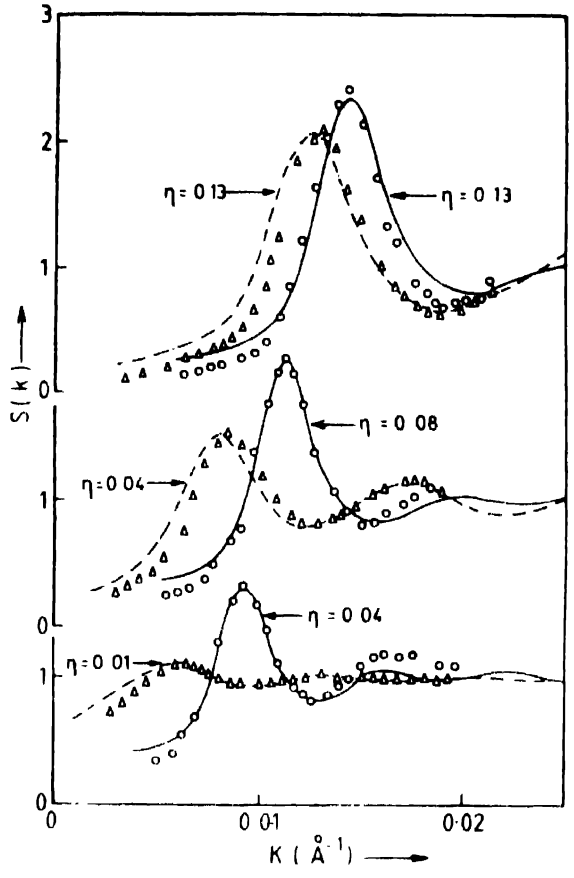

Figure 1 $S(k)$ vs k (Å^{-1}) polystyrene latex. Present calculated results (——) in water and (- - - - -) in 10^{-4} mol dm^{-3} NaCl solution. Experimental results (○○○○) in water, (△△△△) in NaCl solution.

details of different latex volume fraction are given in Table 2. From structure factor $S(k)$, we obtain by Fourier inversion the radial distribution function $g(r)$ and these are shown in Figure 2. The radial features and the co-ordination numbers for the latex particles in water and salt solutions are given in Table 3. The co-ordination number n_i is obtained from the following equation (Rao and Pal 1984)

$$n_i = 4\pi\rho\int_0^{r_{min}} g(r)r^2 dr \tag{10}$$

Table 2 Structural details of polystyrene latex in water and in 10^{-4} mol. dm^{-3} NaCl solution.

Volume fraction (η)	1st maximum				1st minimum			
	Present		Experimental		Present		Experimental	
	position k (Å^{-1})	height $S(k)$	position k (Å^{-1})	height $S(k)$	position k (Å^{-1})	height $S(k)$	position k (Å^{-1})	height $S(k)$
In water								
0 04	0.0093	1.69	0.0092	1.72	0.0132	0.80	0 0128	0 80
0.08	0.0112	2.09	0.0113	2.12	0 0155	0.84	0·0151	0.78
0.13	0.0142	2 32	0.0144	2.35	0.02	0.80	0.0195	0.68
In NaCl								
0.01	0.0060	1.11	0.0066	1.10	0.0096	0.95	0.0098	0 96
0.04	0.0081	1.51	0.0086	1.55	0.0126	0.81	0.0129	0.82
0.13	0·0126	2.08	0.0132	2.21	0.0193	0.72	0.0189	0.68

where r_{min} corresponds to the first minimum in the radial distribution curve. The surface potential of these high polymers which is obtained from the amplitude (A) of VO potential are given in Table 4.

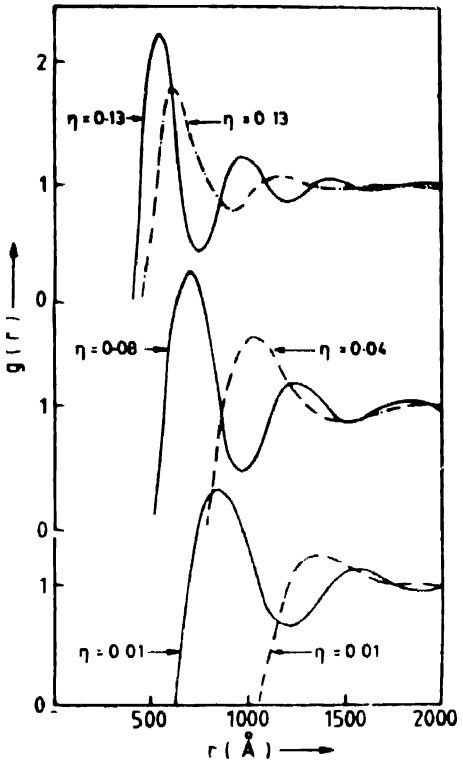

Figure 2 Radial distribution function $g(r)$ vs r (Å) for polystyrene latex (——) in water and (- - - - - -) in 10^{-4} mol dm^{-3} NaCl solution.

Table 3. Structural features of the RDF's and co-ordination number of polystyrene latex in water and in 10^{-4} mol dm^{-3} NaCl solution.

Volume fraction (η)	1st maximum r_{max} (Å)	Height of 1st max $g(r)$	1st minimum r_{min} (Å)	Co-ordination number (n_c)
In water				
0.04	850	1.78	1220	2.84
0.08	680	2.15	960	4.30
0.13	530	2.28	740	6.70
In NaCl				
0.01	1350	1.22	1690	0.88
0.04	1010	1.56	1470	3.95
0.13	590	1.80	904	11.40

3. Results and discussion

From structural studies of the latex solution we have seen (vide Table 1) that the effective diameter σ is found to decrease with increasing volume fraction and this trend was also found by Cebula *et al* (1983) and Ramsay *et al* (1983). It is gratifying to note that the present calculated structure factors of the polystyrene latex in water and in salt solution are found to be in good agreement with the experiment (Cebula *et al* 1983). The potential energy depth (ϵ/k_B) in water and the VO amplitude (A) in salt solution is found to decrease with increasing latex volume fractions. This is expected because with increased concentration (or number density) of the latex the steric hindrance increases with these high polymers having side chains. In general, it is found that the peak height of the structure

Table 4 Surface potential (ψ_s) values of polystyrene latex at different volume fractions (in salt solutions).

Volume fraction (η)	ψ_s (mV)
0.01	101
0.04	97
0.13	70

factor decreases with the addition of salt and the main peak position is found to shift to the left. It may be noticed that the number of nearest neighbours (nnn) is found to increase with the addition of salt (vide Table 3) and further a shift in the peak of the RDF's to the right is observed (vide Figure 2 and Table 3). As the nearest neighbour distance has increased, the effect of salt is repulsive in character. From the amplitude (A) of the VO potential at 0.01 volume fraction, we obtain a value of 101 mV for the surface potential ψ_s. But this value appears to be high with the experimental zeta potential (ξ) value of 58 $\pm$ 10 mV obtained on a very dilute dispersion using laser electrophoresis (Cebula *et al* 1983). However, the present value of 101 mV is better than that obtained by Cebula *et al* (1983) using a hard sphere potential. They obtained a very low value of 20 mV at $\eta=0.01$ which is three times less than the measured value. The discripancy may also be due to the complete inapplicability of VO model itself (Klein and Hess 1983) to produce quantitative results. It may be found from Table 4 that ψ_s value decreases with increasing volume fraction of the latex. The decrease in the surface potential with increased volume fraction can be attributed to the decrease in the charge density. The same trend is also observed by Cebula *et al* (1983). If one has to obtain the exact zeta potential, the σ value should be around 825 Å at $\eta=0.01$ while in the present calculations the σ used is 820 Å (vide Table 1). Thus, it may be concluded that the zeta potential as evaluated from VO potential

is very sensitive to σ [vide eq. (5)]. It is also important to point out at this stage that, macroscopic property namely the surface potential ψ_s is obtained from the microscopic property namely the structure factor $S(k)$, in addition to the facility of evaluation of transport property, like diffusion coefficient of such high polymer system.

4. Conclusion

We conclude that liquid state statistical physics equation can be applied lucratively to high polymer solutions to generate structure factors, and other equilibrium and some non equilibrium properties.

Acknowledgment

One of the authors (D D) is thankful to the U G C and R V G R is grateful to the DST for financial assistance.

References

Ascroft N W and Leckner J 1966 *Phys. Rev* **165** 83

Cebula D J, Goodwin J W, Jeffry C, Ottweill R H, Parentich A and Richardson R A 1983 *Farad. Discuss Chem. Soc* **76** 37

Ise N, Okubo T, Yamamoto K, Kawai H, Hashimoto T, Fujimura M and Hiragi Y 1980 *J. Am Chem. Soc* **102** 7901

Jansen J W, Kruif C G De and Vrij A 1986 *J. Colloid. Intf Sci.* **114** 492

Klein R and Hess W 1983 *Farad Discuss. Chem. Soc* **76** 137

Megen W V and Snook I 1983 *Farad Discuss. Chem Soc.* **76** 151

Nieuwenhuis E A and Vrij A 1979 *J. Colloid Intf Sci.* **72** 321

Ramsay J D F Avery R G and Benest Lance 1983 *Farad. Discuss Chem. Soc* **76** 53

Rao R V G and Murthy A K 1974 *Phys Stat Sol. (b)* **66** 703

1975 *Phys. Lett.* **51A** 3

Rao R V G and Pal S K 1984 *Phys Stat Sol. (a)* **86** 543

Rao R V G and Sen D 1976 *Ind. J. Pure Appl. Phys.* **14** 853

Reddy M C S and Murthy A 1982 *Chem. Phys. Lett* **88** 177

Rouw P W and Kruif C G De 1988 *J. Chem Phys.* **88** 7799

Snook I and Megen W V 1984 *J. Colloid. Intf. Sci.* **102** 446

Thiele E 1963 *J. Chem. Phys* **39** 474

Verwey E J W and Overbeck J T G 1948 *Theory of the stability of Lyophobic Colloids* (Amsterdam : Elsevier)

Wertheim M S 1963 *Phys Rev Lett* **10** 321